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84 Cationic monomer delayed addition process.

37 Water-in-oil emulsions of cationic water-soluble copolymers which are prepared by incorporating only a portion of the cationic monomer in the aqueous phase prior to forming the water-in-oil emulsion in which polymerization will occur, forming the emulsion, adding the balance of the cationic monomer, and then polymerizing the monomers. Copolymers prepared by this new process show improved performance over conventionally prepared cationic copolymers.

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CATIONIC MONOMER DELAYED ADDITION PROCESS

1 This invention relates generally to water-soluble
2 cationic copolymers dispersed in water-in-oil emulsions
3 and an improved process for preparing such copolymers.
4 More particularly, the present invention relates to
5 cationic water-soluble polymers which are prepared by a
6 delayed addition process as specified herein and which,
7 due to the method of preparation, exhibit improved
8 performance characteristics.

9 Water-in-oil emulsions containing cationic water-
10 soluble copolymers dispersed therein are well-known in
11 the art. Such emulsions have found a wide variety of
12 uses, for example, as flocculants in the mining and paper
13 industries and in sewage treatment, and as mobility
14 control agents in enhanced oil recovery. These emulsions
15 have generally been made by dissolving the entire monomer
16 charge in the water and then preparing the water-in-oil
17 emulsion which is the medium in which the polymerization
18 is conducted. This conventional preparation process has
19 been found to generally limit the performance
20 characteristics of the resulting copolymers.

21 One attempt to overcome this problem with cationic
22 copolymers is disclosed in U.S. Patent No. 4,152,200 of
23 A.T. Coscia et al. wherein a portion of the cationic
24 comonomer is withheld from the initial emulsion and then,
25 after polymerization has been initiated, is added incre-
26 mentally. The intent of Coscia et al. appears to be to
27 balance the reactivity ratios of the monomer mixture to
28 take into account the differences in reactivity of the
29 cationic monomer versus the non-ionic comonomer.
30 However, the cationic copolymers produced by Coscia et
31 al., although superior in performance to conventionally
32 prepared polymers, still have insufficient performance
33 characteristics for many uses of cationic copolymers,
34 particularly when used as retention aids for paper or as
35 flocculants for municipal sewage sludge.

1 It is accordingly an object of the present invention
2 to produce water-in-oil emulsions of finely dispersed
3 water-soluble copolymer particles in which the emulsions
4 have improved performance characteristics.

5 It is a further object to develop an improved
6 process for preparing cationic copolymers whereby the
7 surfactant and/or oil contents may be reduced below those
8 amounts conventionally used.

9 It is a further object to develop an improved paper
10 retention aid.

11 It is a further object to develop an improved
12 flocculant for sludge dewatering.

13 These and other objects will become apparent from
14 the ensuing description.

15 In accordance with the present invention, there is
16 provided an improved process of preparing water-in-oil
17 emulsions of water-soluble cationic copolymers which
18 comprises (i) preparing an aqueous solution of a
19 water-soluble non-ionic monomer and from about 5 to about
20 85 weight percent of the total quantity of a cationic
21 monomer to be incorporated, (ii) emulsifying the aqueous
22 solution in a sufficient quantity of a hydrocarbon oil to
23 form a water-in-oil emulsion, (iii) adding the balance of
24 the cationic monomer to the water-in-oil emulsion, and
25 (iv) polymerizing the monomers to form a cationic
26 water-in-oil emulsion copolymer. The copolymers so
27 produced differ from copolymers prepared by other
28 processes in that they exhibit improved performance
29 characteristics.

30 The cationic copolymers of the present invention are
31 comprised of at least 30 mole percent of repeating units
32 derived from a water-soluble nonionic monomer and
33 repeating units derived from a cationic monomer.
34 Suitable nonionic water-soluble monomers include
35 acrylamide, methacrylamide, N-methylacrylamide,
36 N-methylmethacrylamide, diacetone acrylamide, and the

1 like. Suitable cationic monomers include the metho-
2 sulfate or methylchloride quaternaries of such as
3 dimethylaminoethylacrylate, dimethylaminoethylmeth-
4 acrylate, diethylaminoethylacrylate, and diethyl-
5 aminoethylmethacrylate, as well as 3-(methylacrylamido)-
6 propyltrimethylammonium chloride, diallyldimethylammonium
7 chloride, 1-trimethylammonium-2-hydroxypropylmethacrylate
8 methosulfate, and the like.

9 Other comonomer units may also be present in minor
10 amounts in the copolymers. They may be either water-
11 soluble or water-insoluble provided that the final
12 copolymer is still water-soluble, i.e. the polymer is
13 soluble in water in an amount of at least 1% by weight.
14 If the other comonomer units are anionic, the mole
15 proportion thereof should be less than or equal to that
16 of the cationic comonomer so that the resulting polymer
17 ionicity is neutral or cationic. Suitable other monomers
18 include anionic, neutral, and amphoteric monomers which
19 may be water-soluble or water-insoluble. Examples of
20 these and other suitable monomers include acrylic acid
21 and its salts, methacrylic acid and its salts, vinyl
22 acetate, methyl acrylate, ethyl acrylate,
23 betacarboxyethyl acrylate, propyl acrylate, methyl
24 methacrylate, ethyl methacrylate, maleic acid and its
25 salts, hydroxyethyl acrylate, hydroxyethyl methacrylate,
26 styrene, acrylonitrile, 2-acrylamido-2-methylpropane
27 sulfonic or phosphonic acid and their salts, dimethyl-
28 aminopropylmethacrylamide, isopropylaminopropylmethacryl-
29 amide, methacrylamidopropylhydroxyethyltrimethylammonium
30 acetate, vinyl methyl ether, vinyl ethyl ether, vinyl
31 sulfonic acid and its salts, vinyl pyridine, vinyl
32 pyrrolidone, vinyl imidazole, styrene sulfonic acid and
33 its salts, and the like.

34 The copolymers produced herein will comprise at
35 least about 30 mole percent water-soluble nonionic
36 monomer units, about 1 to 70 mole percent cationic

1 monomer units, and the balance, if any, of such other
2 monomer units such that the copolymer is water-soluble.
3 Preferably, the copolymer will contain at least about 50
4 mole percent water-soluble nonionic monomer units and,
5 most preferably, those units will be derived from acryl-
6 amide.

7 Although the present invention has been found to be
8 independent of the particular emulsion polymerization
9 method employed provided that a portion of the cationic
10 monomer is added after the emulsion is formed, certain
11 preferences are delineated in the general description of
12 the emulsion preparation which follows:

13 A preliminary emulsion is made by homogenizing oil
14 and aqueous phases. The oil phase of the emulsion, which
15 generally comprises from about 5 to 35 percent by weight
16 of the total emulsion, is comprised of one or more inert
17 hydrophobic liquids. Preferably, the oil phase comprises
18 about 15 to 30 percent of the emulsion. The oil used may
19 be selected from a large class of organic liquids which
20 are immiscible with water, including liquid hydrocarbons
21 and substituted liquid hydrocarbons. Representative
22 examples of such oils include benzene, xylene, toluene,
23 mineral oils, kerosenes, naphthas, chlorinated hydrocar-
24 bons, such as perchloroethylene, and the like.

25 The oil phase also contains the primary surfactants,
26 i.e. conventional emulsion polymerization stabilizers.
27 Such stabilizers are well known to the art to promote the
28 formation and stabilization of water-in-oil emulsions.
29 Normally such emulsifiers have HLB values in the range of
30 about 2 to about 10, preferably less than about 7.
31 Suitable such emulsifiers include the sorbitan esters,
32 phthalic esters, fatty acid glycerides, glycerine esters,
33 as well as the ethoxylated versions of the above and any
34 other well known relatively low HLB emulsifier. Examples
35 of such compounds include sorbitan monooleate, the
36 reaction product of oleic acid with isopropanolamide,

1 hexadecyl sodium phthalate, decyl sodium phthalate,
2 sorbitan stearate, ricinoleic acid, hydrogenated ricin-
3 oleic acid, glyceride monoester of lauric acid, glyceride
4 monoester of stearic acid, glycerol diester of oleic
5 acid, glycerol triester of 12-hydroxystearic acid,
6 glycerol triester of ricinoleic acid, and the ethoxylated
7 versions thereof containing 1 to 10 moles of ethylene
8 oxide per mole of the basic emulsifier. Thus any emul-
9 sifier may be utilized which will permit the formation of
10 the initial emulsion and stabilize the emulsion during
11 the polymerization reaction.

12 These primary surfactants are used alone or in
13 mixtures and are utilized in as low amounts as is
14 possible since an excess will not only increase the cost
15 of the resultant emulsion but may also reduce the per-
16 formance. As such, all of the primary surfactants should
17 together be used in amounts not greater than about 5% by
18 weight of the total emulsion. Preferably the amount is
19 not greater than 3%, and most preferably it is less than
20 about 2.5%.

21 The aqueous phase generally comprises about 95 to 65
22 percent by weight of the emulsion. Preferably, it
23 comprises about 85 to 70 percent thereof. In addition to
24 water, the aqueous phase contains the monomers being
25 polymerized, except for the portion (about 5 to 85%
26 preferably about 30 to 75%, and most preferably about 45
27 to 70%, all by weight) of the cationic monomer which is
28 withheld, generally in an amount of less than about 45
29 percent, preferably about 20 to about 40 percent and most
30 preferably about 25 to about 35 percent, by weight of the
31 total emulsion, and generally chain transfer agents,
32 initiators and sequesterants. Alternatively, the chain
33 transfer agents, initiators and sequesterants may be
34 added to the system after the preliminary emulsion has
35 been prepared. The initiator may also be added continu-
36 ously during the polymerization to control the rate of

1 polymerization depending upon the particular monomers
2 used and their reactivities. All of these variations are
3 well known in the art.

4 Any conventional chain transfer agent may be em-
5 ployed, such as propylene glycol, isopropanol, 2-mercap-
6 toethanol, sodium hypophosphite, dodecyl mercaptan and
7 thioglycolic acid. The chain transfer agent is generally
8 present in an amount of about 0.1 to 10 percent by weight
9 of the total emulsion, though more may be used.

10 The initiator may be any free radical producing
11 material well known in the art. The preferred free
12 radical initiators are the redox-type and the azo-type
13 polymerization initiators and they are generally used
14 either individually or in any combination in an amount of
15 about 0.0005 to 0.5 percent by weight of the total
16 emulsion. Radiation may also be used to initiate the
17 reaction.

18 Any conventional sequesterant may also be present in
19 the aqueous phase, such as ethylenediaminetetraacetic
20 acid or pentasodium diethylenetriamine pentaacetate. The
21 sequesterant is generally present in an amount of about
22 0.01 to 2 percent by weight of the total emulsion, though
23 more may be utilized.

24 Following preparation of the preliminary emulsion,
25 the balance of the cationic monomer is added rapidly and
26 with stirring. The addition rate has not been found to
27 be critical but it must not be so fast as to destabilize
28 the preliminary emulsion, nor so slow as to permit auto-
29 catalysis. The polymerization is then commenced in
30 accordance with standard techniques. Preferably, the
31 preliminary emulsion is heated to about the desired
32 polymerization temperature prior to the addition of the
33 balance of the cationic monomer. The heating may be
34 accomplished by an external heating mechanism. More
35 preferably, it is done by initiating polymerization of
36 the monomers in the primary emulsion, allowing the

1 temperature to rise to the desired level, and then
2 suspending or quenching the polymerization until after
3 the balance of the cationic monomer has been added. The
4 quenching may be accomplished by such as eliminating the
5 sustaining catalyst feed or deliberately adding oxygen to
6 the reaction. In this case, the rate of polymerization
7 is effectively zero when the remaining cationic monomer
8 is added, and then the polymerization is re-initiated.
9 The cationic monomer may be added neat, though it is
10 generally dissolved in water or even in the aqueous phase
11 of a secondary water-in-oil latex. When a secondary
12 latex is used, the total amount of oil and primary
13 surfactants has been found to be reduced from that which
14 would conventionally be used. The cationic monomer may
15 be treated to remove the polymerization inhibiting
16 oxygen, but this has not been found to be necessary.

17 The polymerization is generally run at a temperature
18 of about -20°C to 200°C , preferably at about 0°C to
19 100°C , and most preferably at about 35°C to 75°C .

20 Preferably the polymerization is run at a pH of
21 about 2 to 12 and a suitable amount of base or acid may
22 be added to the preliminary emulsion to achieve the
23 desired pH. The polymerization is usually completed in
24 about an hour or two to several days, depending upon the
25 monomers employed and other reaction variables. It is
26 generally carried out at atmospheric pressure, but higher
27 pressures are advantageously used when volatile ingre-
28 dients are involved.

29 Following completion of the polymerization, the pH
30 of the emulsion may be adjusted as desired. For an
31 anionic polymer emulsion, this is generally about 4 to
32 10; for cationic emulsions about 2.0 to 7.0; and for
33 non-ionic emulsions about 2.0 to 8.0. A breaker surfac-
34 tant is generally added to yield a self-inverting final
35 product. Any suitable breaker surfactant may be
36 employed, experimentation being the best means of

1 determining which breaker surfactant will perform
2 optimally with a given emulsion system. Typical breaker
3 surfactants include those having relatively high HLB
4 numbers such as ethoxylated octyl and nonyl phenols,
5 ethoxylated nonyl phenol formaldehyde resin, polyethylene
6 oxide esters of fatty acids, dioctyl esters of sodium
7 sulfosuccinate and others disclosed in U.S. 3,624,019
8 incorporated herein by reference.. Typically, the breaker
9 surfactant is added in an amount equal to about 0.5 to 5
10 percent by weight, based on the total emulsion. Prefer-
11 ably the amount is less than 3 percent and most prefer-
12 ably less than about 2.5 percent.

13 Once prepared, the emulsions of the present inven-
14 tion may be chemically modified in any known manner.
15 "Chemically modified" is intended to cover further
16 treatment of the dispersed water-soluble polymer and/or
17 the addition of components to the dispersed water-soluble
18 polymer which, without the stabilization provided by the
19 emulsion stabilizers, would cause the normally water-
20 soluble polymeric particles to coagulate or agglomerate.
21 Examples of such further treatments are disclosed in U.S.
22 Patent Nos. 4,052,353 and 4,171,296, incorporated herein
23 by reference. The emulsion of the present invention may
24 also be concentrated in any suitable manner, such as is
25 disclosed in U.S. Patent No. 4,021,399, incorporated
26 herein by reference.

27 When the cationic copolymer emulsions of the present
28 invention are utilized as retention aids for paper, they
29 are added to the paper furnish at the wet end of the
30 paper machine in typical amounts such as about 0.1 to
31 about 15.0 pounds of active polymer per ton of finished
32 paper. When they are used for flocculation in sludge
33 dewatering, they are used in conventional amounts, i.e.
34 about 1 to about 500 ppm on a sludge containing about 1
35 to 5% of suspended material.

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1 The following examples are illustrative of the
2 present invention, but are not in any way a limitation
3 thereof. All parts are by weight unless otherwise
4 specified.

5 Comparative Example A

6 A water phase containing 260 g. of acrylamide, 90 g.
7 of dimethylaminoethylmethacrylate methyl chloride
8 quaternary 1.2 g. of ethylenediaminetetraacetic acid, 0.5
9 g. of potassium bromate, and 331.6 g. of water is
10 homogenized with an oil phase containing 220 g. of oil,
11 14.5 g. of ricinoleic acid triglyceride ester which has
12 been hydrogenated and ethoxylated with five moles of
13 ethylene oxide, and 4.8 g. of sorbitan monooleate. The
14 resulting emulsion system is then transferred to a
15 suitable reaction vessel with stirring and sparged with
16 nitrogen. 30.0 g. of a 4.5% solution of sodium bisulfite
17 is added continuously during the polymerization and the
18 temperature of the emulsion increases to about 35-45°C.
19 Cooling is provided to maintain this temperature and
20 agitation is maintained for 4-10 hours. The polymeriza-
21 tion is completed at the end of that time and results in
22 an 8 mole % cationic polyacrylamide emulsion having 35
23 percent polymer solids.

24 Example I

25 The procedure of Comparative Example A was repeated
26 except that 56.3 g. of the cationic monomer
27 dimethylaminoethylmethacrylate methyl chloride quaternary
28 was omitted in preparing the initial water-in-oil
29 emulsion. The initial emulsion was then heated to 40°C
30 via external heating and the omitted cationic monomer was
31 added in the form of an 80% solution within about thirty
32 minutes. Thereafter, polymerization proceeded with the
33 commencement of the bisulfite addition as in Comparative
34 Example A.

Comparative Example B

The procedure of Example I was repeated except that the omitted cationic monomer was added after the polymerization had been commenced and the temperature had increased to 40°C. It was added continuously during the polymerization as described in U.S. Patent 4,152,200.

Example II

In order to determine the performance characteristics of the cationic copolymers prepared in each of Comparative Examples A and B and Example I, the emulsions were evaluated as retention aids on paper mill furnish. The testing was performed using a conventional Britt Jar procedure. The average results of several replications are given in Table I which follows:

Table IRetention Aid Evaluation

<u>Polymer of</u> <u>Example</u>	<u>Dosage,</u> <u>\$/ton active</u>	<u>% First Pass</u> <u>Retention Ash</u>	<u>% First Pass</u> <u>Retention Total</u>
Comparative A	1.0	24	60
Comparative B	1.0	32	60
I	1.0	37	67
Comparative A	1.5	35	62.5
Comparative B	1.5	41.5	64
I	1.5	47	72
Comparative A	2.0	38.5	65
Comparative B	2.0	48	66.5
I	2.0	52	74.5

As can be seen, in each case the polymer of the present invention clearly outperformed the polymers prepared by prior art methods.

Example III

The procedure of Example I to produce an emulsion was repeated except that the cationic monomer was changed

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1 to dimethylaminoethylmethacrylate methosulfate quater-
 2 nary, which is generally known to produce a less effec-
 3 tive retention aid. However, unexpectedly, when the
 4 Britt Jar evaluation of Example II was conducted with
 5 this copolymer the results were even superior to those
 6 observed with the copolymer of Example I, as can be seen
 7 in Table II below:

8 Table II
 9 Results of Example III

10	Dosage,	% First Pass	% First Pass
11	<u>\$/ton active</u>	<u>Retention of Ash</u>	<u>Retention Total</u>
12	1.0	40	68
13	1.5	50.5	74
14	2.0	57	78

15 Example IV

16 The procedure of Example I was repeated except that
 17 instead of using external heating to increase the tem-
 18 perature to 40°C before adding the omitted cationic
 19 monomer, polymerization of the emulsion was instigated by
 20 commencing the addition of sodium bisulfite. When the
 21 temperature reached 40°C, (about less than 5% monomer
 22 conversion) the bisulfite addition was stopped and the
 23 reaction was terminated by oxygen quenching, i.e. essen-
 24 tially no polymerization was occurring. At this point,
 25 the omitted cationic monomer was added within about 30
 26 minutes. After the addition was complete, the reactor
 27 was purged with nitrogen, the bisulfite feed was restart-
 28 ed and polymerization continued until the reaction was
 29 complete. When tested as a retention aid as in Example
 30 II, substantially equivalent results to those of Example
 31 I were observed.

1 Comparative Example C

2 The procedure of Example IV was repeated except that
3 all of the cationic monomer was placed in the initial
4 emulsion and none was added during the 30 minutes the
5 reaction was stopped. When tested as a retention aid as
6 in Example II, substantially equivalent results to those
7 of Comparative Example A are observed.

8 Example V

9 The procedure of Example I was repeated except that
10 thirty percent of the water-in-oil emulsion forming
11 ingredients, i.e. water, oil, ricinoleic acid ester and
12 sorbitan monooleate, was omitted from primary water-in-
13 oil emulsion and the omitted cationic monomer was added
14 in the water phase of a water-in-oil emulsion which
15 contained the omitted thirty percent of the emulsion
16 forming ingredients. When tested as a retention aid as
17 in Example II, substantially equivalent results to those
18 of Example I were observed.

19 Example VI

20 The procedures of Comparative Example A and then
21 Example I was repeated except that (i) the cationic
22 monomer was replaced with dimethylaminoethylmethacrylate
23 methosulfate quaternary and the amount was increased to
24 20 mole percent, (ii) sorbitan monooleate was used as the
25 sole surfactant, and (iii) the catalyst system was
26 replaced with 2,2'-azobis(isobutyronitrile) which was
27 added incrementally during the polymerizations.

28 In order to evaluate the performance characteristics
29 of the resultant polymers in sludge dewatering, a series
30 of conventional Buchner Funnel tests were performed on
31 sludge from the City of Detroit sewage treatment plant.
32 The tests are performed by taking a representative sludge
33 sample, dividing it into aliquots, adding the desired
34 amount of polymer being tested, conditioning the sludge

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1 by mixing the polymer solution in the sludge for 15
2 seconds at 450 rpm, pouring the conditioned sludge into a
3 Buchner Funnel with moist filter paper, and then deter-
4 mining the drainage for a given period of time. The
5 results of the tests are shown in Table III below.

6 Table III
7 Sludge Dewatering Evaluation
8 Drainage in Milliliters

	<u>Dosage</u>	<u>Polymer</u>	
		<u>Comparative</u>	<u>Invention</u>
11	<u>#/ton</u>		
12	20	49-95	113-117
13	30	70-103	125-131
14	40	63-92	136-140
15	45	47-73	138-141

CLAIMS

1. A method of preparing a water-soluble cationic copolymer, which is composed of at least 30 mole percent of repeating units derived from a water-soluble nonionic monomer and repeating units derived from a cationic monomer, which comprises the steps of (i) preparing an aqueous solution of the nonionic monomer and from about 5 to 85 weight percent of the cationic monomer, (ii) emulsifying the aqueous solution in a sufficient quantity of hydrocarbon oil to form a water-in-oil emulsion, (iii) adding the balance of the cationic monomer to the emulsion while essentially no polymerisation is occurring and (iv) polymerising the monomers.
2. The method of Claim 1 wherein prior to adding the balance of the cationic monomer the temperature of the emulsion is increased to about the desired polymerisation temperature.
3. The method of Claim 1 or Claim 2 wherein the temperature is increased by external heating.
4. The method of any of the preceding claims wherein the temperature is increased by initiating polymerisation of the monomers and then suspending the polymerisation during the addition of the balance of the cationic monomer.
5. The method of any of the preceding Claims wherein the nonionic monomer is selected from the group consisting essentially of acrylamide, methacrylamide, N-methylacrylamide, diacetoneacrylamide, and N-methylmethacrylamide.

6. The method of any of the preceding claims wherein the cationic monomer provides 1 to 70 mole percent of the repeating units and is selected from the group consisting essentially of 3-methylacrylamido-propyltrimethylammonium chloride and the methosulfate and methylchloride quaternaries of dimethylamino-ethylacrylate, dimethylaminoethylmethacrylate, diethylaminoethylacrylate and diethylamino-ethylmethacrylate.
7. The method of any of the preceding claims further containing minor amounts of repeating units derived from monomers selected from the group consisting essentially of anionic monomers and nonionic water-insoluble monomers.
8. The method of any of the preceding claims wherein the balance of the cationic monomer is added as an aqueous solution.
9. The method of any of the preceding claims wherein the balance of the cationic monomer is added as a latex in the aqueous phase of a water-in-oil emulsion.
10. The method of any of the preceding claims wherein the balance of the cationic monomer is about 30 to 75 weight percent of the total cationic monomer being polymerised.
11. A water-in-oil emulsion whenever prepared by a process according to any one of the preceding claims.

12. The use as a retention aid for paper of a water-in-oil emulsion according to Claim 11.
13. The use according to Claim 12 in amounts of about 0.1 to 15.0 pounds of active polymer per ton of finished paper.
14. A retention aid for paper comprising a copolymer prepared according to any of Claims 1 to 10.
15. A flocculant comprising a copolymer prepared according to any of Claims 1 to 10.
16. The use of the flocculant of Claim 15 for sludge dewatering.
17. The use according to Claim 16 wherein the flocculant is used in an amount of 1 to 500 ppm when the sludge contains 1 to 5% by weight of suspended material.